

MONAZITE BASED BLANKET COATINGS FOR THERMAL PROTECTION SYSTEMS

CROSS-REFERENCE TO RELATED APPLICATIONS

5 **[0001]** This application is a divisional application of United States Patent Application No. 09/883,760 filed on June 18, 2001, now patent number 6,716,407. The disclosure of which is incorporated herein by reference.

FIELD OF THE INVENTION

10 **[0002]** The present invention relates to ceramic composites and, in particular, to high temperature ceramic composites comprising monazites.

BACKGROUND OF THE INVENTION

15 **[0003]** Thermal protection (i.e., heat shields) for reentry vehicles, such as the Space Shuttle, are traditionally assembled of ceramic tiles over the vehicle surface. The tiles are of relatively small area to fit the compound curves and are costly to fabricate and to bond to the surface. Upon reentry, tiles often are damaged which results in a labor-intensive, time consuming replacement operation. With the goal of quick turnaround for reuse of spacecraft, tiles are ineffective.

20 **[0004]** Insulating blankets made from ceramic fibers show promise, but they are used sparingly because traditional blankets made entirely from silica quickly deteriorate upon exposure to high temperatures in an oxidative environment. The blankets are initially flexible and are relatively easy to apply, but they rapidly become brittle. The lack of toughness caused by embrittlement makes the blankets
25 susceptible to damage and forces their replacement. These silica blankets have a reuse temperature of only about 1200°F. Replacing a blanket requires destroying the original blanket to remove it from the spacecraft surface, cleaning the spacecraft surface to prepare the surface for rebonding a new blanket, fabricating a replacement blanket, and positioning and adhesively bonding the replacement blanket to the
30 surface. The delay associated with the curing of the traditional RTV silicone adhesive is up to seven days, which is unacceptable for a reusable launch vehicle where rapid turnaround is necessary for economic success.

[0005] Silica coated blankets have also been tried, but they have achieved limited success. Silica coatings are incompatible with many high temperature ceramics, including alumina, aluminosilicate, or aluminoborosilicate (e.g., Nextel[®]), so the silica approach has only limited applicability.

5 [0006] Today, coated blankets must be able to withstand reentry temperatures of at least 1800-2300°F. while remaining tough and flexible. The blankets should be fastenable to the surface and removable, somewhat like conventional access panels, for servicing the vehicle or for quick replacement of the insulation when it becomes damaged. Therefore, a coating solution for the blanket fibers must retain the flexibility
10 of the fabric while deterring embrittlement upon exposure to temperatures in the 2000°F range.

SUMMARY OF THE INVENTION

[0007] The present invention provides monazite- or xenotime-based coatings
15 that stiffen ceramic fabrics without causing embrittlement at temperatures of at least as high as 2400°F. In one embodiment the coatings comprise high purity, stoichiometric monazite powders. The high purity monazite powders have low-level impurities and excess phosphate and/or phosphorous removed, providing a superior coating for use at temperatures above 2000°F. In another embodiment, the coatings further comprise
20 SiC additives to increase emissivity.

[0008] The present invention also provides methods for the synthesis of high purity, stoichiometric monazite powders for use in blanket coatings. In one embodiment the methods comprise forming a monazite by precipitation from an aqueous solution. The monazite phosphate is then washed with water followed by a
25 strong base. The washing step removes low levels of impurities and excess phosphate and/or phosphorous which effect the thermal stability of the coatings.

[0009] Additional objects, advantages, and features of the present invention will become apparent from the following description and appended claims.

[0010] Further areas of applicability of the present invention will become
30 apparent from the detailed description provided hereinafter. It should be understood

that the detailed description and specific examples are intended for purposes of illustration only and are not intended to limit the scope of the invention.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

5 **[0011]** The following description of the preferred embodiment(s) is merely exemplary in nature and is in no way intended to limit the invention, its application, or uses.

10 **[0012]** The present invention provides high temperature monazite- or xenotime-based coatings that infiltrate and stiffen ceramic fabrics without causing embrittlement at temperatures at least as high as 2400° F. In one embodiment, the coatings comprise high purity, stoichiometric monazite or xenotime powders. Monazite comprises a family of phosphates having the general formula MPO_4 (MP), where M is selected from the larger trivalent rare earth elements of the lanthanide series (generally La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, and Tb) and coupled substituted divalents and
15 tetraivalents such as Ca or Sr with Zr or Th. Xenotimes are phosphates similar to monazite, where M is selected from Sc, Y, and the smaller trivalent rare earth elements of the lanthanide series (generally Dy, Ho, Er, Tm, Yb, and Lu). In a preferred embodiment, the monazite powder is selected from the group comprising lanthanide (La), cerium (Ce) or yttrium (Y). More preferably, the monazite powder is $LaPO_4$.

20 **[0013]** In another embodiment, the monazite powder is basically free of impurities and excess phosphorous. In a preferred embodiment, the monazite powder has a stoichiometry of $M:PO_4$ of about 1:1 to about 1:1.05. It has been unexpectedly found that blanket coatings comprising this high purity monazite powder produce a coating on a ceramic blanket that is stable and less susceptible to cracking at
25 temperatures of at least 2400°F. Ceramic fabrics coated with monazite-based coatings that contained low levels of impurities and excess phosphorous exhibited degradation in the retained fiber strength when exposed to similar temperatures.

30 **[0014]** In one embodiment, the monazite-based coatings comprise a high purity monazite powder and alumina (Al_2O_3). It is contemplated that coatings using monazite powders containing more impurities and alumina can also be used with the high purity monazite powders of the present invention. Non-limiting examples of such

coatings are disclosed in U.S. Patent Nos. 5,514,474 and 5,958,583, hereby incorporated by reference. In a further embodiment, the coatings also comprise SiC additives. Such additives help to increase the emissivity. In yet another embodiment, the coatings of the present invention further comprise small diameter chopped fibers. Such fibers are present at an amount not greater than about 10% of the total solids volume. Addition of such fibers are well known to the skilled artisan.

[0015] Methods for synthesizing high purity, stoichiometric monazite powders are also provided by the present invention. In one embodiment the monazites or xenotimes are formed by precipitation from an aqueous solution. Water soluble lanthanide salts and either phosphate salts or phosphoric acid are dissolved in water. In a preferred embodiment, the lanthanide salt is lanthanum nitrate and phosphoric acid is the phosphate. The monazites and xenotimes formed in solution are water-insoluble and will precipitate out. The precipitated monazite or xenotime exhibit a pronounced needle-like morphology. This microstructure is advantageous for washing the precipitate to remove impurities and excess phosphate and/or phosphorous. In another embodiment, the precipitate is washed with water followed by a strong base. Preferably the strong base is tetramethylammonium hydroxide. Washing with a strong base especially removes any excess phosphate and/or phosphorous resulting in a monazite with a stoichiometry of $M:PO_4$ of about 1:1. It will be appreciated that one skilled in art can determine the volume of wash solutions necessary depending on the amount of precipitate formed to produce the monazite powders of the present invention.

[0016] In a further embodiment, the washed precipitate are first calcined to coarsen them slightly and to bond the needles together. The calcined precipitate is then dispersed in water at the proper pH and attritor milled to de-agglomerate the particles and reduce the grain size. In a preferred embodiment, the resulting powders have a particle size of about 100 nm to about 500 nm.

[0017] The monazite and xenotime powders produced by the methods of the present invention were used to produce aqueous slurries for fabric coupon coatings. Nextel[®] 440 blanket coatings were produced from an aqueous-based slurry (15-25 vol% solids) comprising 42.4% $LaPO_4$, 42.4%, Al_2O_3 and 15.2% SiC. After the

slurry was thoroughly mixed, NH_4OH was added dropwise until the pH reached approximately 7. The slurry was then ball milled for approximately 12 hours and painted onto the blanket fabric using a boxcoat pattern. The coated blankets were dried thoroughly prior to heat treatment.

5 **[0018]** Although the present invention has been described with respect to specific embodiments thereof, various changes, modifications, and substitutions may be suggested to one skilled in the art. Therefore, it is intended that the present invention encompass such changes and modifications as falling within the scope of the appended claims.

10 **[0019]** While various preferred embodiments have been described, those skilled in the art will recognize modifications or variations which might be made without departing from the inventive concept. The examples illustrate the invention and are not intended to limit it. Therefore, the description and claims should be interpreted liberally with only such limitation as is necessary in view of the pertinent prior art.